Lepidoptera and plant hosts. Finally, the presence of this pair of forms now restricted to the tropics and subtropics reinforces the impression from the total Wind River flora (15) that this area of the central Rocky Mountains was subject to a humid, subtropical climate in the late early Eocene.

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## Jupiter: Its Infrared Spectrum from 16 to 40 Micrometers

Abstract. Spectral measurements of the thermal radiation from Jupiter in the band from 16 to 40 micrometers are analyzed under the assumption that pressure-broadened molecular hydrogen transitions are responsible for the bulk of the infrared opacity over most of this spectral interval. Both the vertical pressure-temperature profile and the molecular hydrogen mixing ratio are determined. The derived value of the molecular hydrogen mixing ratio,  $0.89 \pm 0.11$ , is consistent with the solar value of 0.86.

The abundance of  $H_2$  and He in the Jovian atmosphere has a direct influence on a number of astronomical problems. Jupiter's low atmospheric temperature and great mass prevent even the lightest atoms from escaping from the top of the atmosphere. Therefore, Jupiter as a whole is a sample of the elemental abundance at the time of the formation of the planet. Modern theories of explosive nucleosynthesis show that most of the He presently in the universe was formed during the Big Bang (1). Further, it has been shown that the relative abundance of H<sub>2</sub> and He depends strongly on the temperature and density during the early stages of the evolution. To the extent that the Jovian atmosphere is representative of the planet as a whole, a measure of the H<sub>2</sub> mixing ratio  $\alpha_{\rm H_2}$  =  $N(H_2)/[N(H_2) + N(He)]$ , where N(x) is the number density of x in the atmosphere, is useful for the determination of the conditions during the early stages of the Big Bang. There are, however, several effects which may systematically distort the atmospheric value of  $\alpha_{\rm H_2}$ .

Opik has suggested a model for the for-

mation of Jupiter in which first "hydrogen snow" collects to form a core and then a He-rich atmosphere is captured (2). Salpeter has suggested that there may be internal differentiation with the He sinking toward the center of the planet, resulting in a  $H_2$ -rich atmosphere (3).

We observed Jupiter on the nights of 14 November and 16 November 1973 and 21 January 1974, using a 31-cm telescope mounted on the National Aeronautics and Space Administration Ames Research Center Lear jet. The aircraft was flown to an altitude of 14 km (45,000 feet). At this altitude about 3 to 10 precipitable micrometers of water remain above the observer. The telescope viewed the source at elevation angles between 14° and 28°. The spectral scans were made with two different grating spectrometers cooled to liquid helium temperatures (4). These instruments employ an Ebert-Fastie spectrometer (12.5-cm focal length) with two detectors in the focal plane. Instrument 1 has a Ge: Cu photoconductor to scan the 16to 28- $\mu$ m band, and a Ge: Ga photoconductor covers the range from 20 to 40  $\mu$ m. The resolution of the two channels is 0.5 and 1.0 µm, respectively. Instrument 2 has two Ge: Cu photoconductors and covers the range from 16 to 28  $\mu$ m with a 2.7-mm entrance aperture corresponding to 4.7 minutes of arc. Jupiter had a diameter of about 0.5 minute of arc during the observing periods. The chopping frequency was 48 hertz.

We determined the instrumental response by normalizing spectra of the moon and Mars as if they were blackbody radiators at 350° and 240°K, respectively. The instrumental profile determined in this way is consistent with the laboratory profile and the absorption expected by the atmosphere. It was used to normalize the Jupiter data. The resulting spectrum (Fig. 1a) shows the presence of three absorption features at 18, 23.5, and 28 µm. The first and last are, respectively, the J = 1 and J = 0rotational transitions of H<sub>2</sub>. The 23.5-  $\mu$ m feature shown in Fig. 1a may be due to sulfur, silicate dust, or complex hydrocarbons in the atmosphere (5). However, recent data of greater resolution and signal-to-noise ratio indicates that the brightness temperature falls smoothly from a maximum at 21  $\mu$ m to a broad minimum around 28  $\mu$ m. The regions of the spectrum used to determine the ratio of  $H_2$  to He are substantially unchanged. However, the reality of the 23.5  $\mu$ m is somewhat in doubt. A discussion of all the observational data will be given by Pollack et al. (6).

The observed spectrum of Jupiter contains information about both a portion of its vertical temperature structure and its ratio of He to  $H_2$ . Before describing our numerical method for deriving this information, we describe the physical connection between these quantities and the observed spectrum. The brightness temperature found at a given wavelength is approximately equal to the value of the physical temperature in the Jovian atmosphere at an optical depth of unity. As the wavelength changes, the altitude at which the optical depth is unity also varies. Thus, spectral observations over a range of wavelengths provide information on the temperature conditions over a corresponding range of altitudes in the atmosphere. For the spectral band measured, H<sub>2</sub> is the principal source of opacity. The Jovian atmosphere is probed from pressures of about 0.15 to 0.6 atm, a region which includes a temperature minimum and the top of the convection zone.

In carrying out the analysis described below, we excluded data close to the 23.5- $\mu m$  feature. In addition to opacity due to the rotational and translational transitions of H<sub>2</sub>, we allowed for opacity due to NH<sub>3</sub>, which is important only at the longwavelength edge of our data. We carried



Fig. 1. (a) The brightness temperature of Jupiter for wavelengths from 16 to 40  $\mu$ m. (b) The pressure-induced absorption coefficients for H<sub>2</sub>-He collisions. The curves shown represent the sums of both translational and rotational transitions.

out calculations both without and with an optically thick  $NH_3$  cloud present in the zone regions of Jupiter, located at the level of the atmosphere where  $NH_3$  saturation occurs. The  $NH_3$  clouds were assumed to behave as blackbody emitters.

In accord with radio temperature measurements we assumed that the temperature gradient equaled the adiabatic value at pressures greater than the bottom altitude boundary of the region we sense (7). Our derived temperature profiles are consistent with this assumption. Above our top altitude boundary we made use of the temperature gradients derived by Orton (8) from an analysis of measurements in the region of the 7.7-  $\mu$ m CH<sub>4</sub> band.

Our ability to gain information about the ratio of He to  $H_2$  follows from the dependence of the pressure-induced transitions of  $H_2$  on this ratio. This dependence is illustrated in Fig. 1b, which shows the values of the absorption coefficient of  $H_2$ when the rotational transitions occur in the presence of a nearby molecule of  $H_2$  ( $H_2$ - $H_2$ ), and in the presence of a nearby He atom ( $H_2$ -He). We see from Fig. 1b that the absorption coefficient shows a different spectral variation for the ( $H_2$ -He) case than for the ( $H_2$ -H\_2) case.

The numerical method used to obtain the desired information from the observed spectrum of Jupiter begins with an assumed trial value of  $\alpha_{H_2}$ . For this choice of the mixing ratio, the observed spectrum is inverted to determine the pressure-temperature structure by means of an iteration technique developed by Smith (9) and applied to planetary atmospheres by Ohring (10). This method is similar to the method 29 AUGUST 1975 developed by Encrenaz and Gautier (11) and Gautier and Grossmann (12). It involves starting with a trial temperature profile, computing a predicted spectrum with this profile, and correcting the profile on the basis of the difference between the observed and calculated flux values, the flux residuals. The improved guess is used to repeat this process and, after a small number of iterations, the root-meansquare of the flux residuals approaches an asymptotic value. This procedure is repeated for other trial values of  $\alpha_{H_2}$ . An estimate of  $\alpha_{\rm H_2}$  was obtained from the locations of the minimum in the value of the flux residual as a function of mixing ratio

Figure 2 shows the vertical temperature structure of Jupiter determined from our spectrum for  $\alpha_{\rm H}$ , values of 0.8 and 1.0. These results refer to models containing no NH, cloud opacity. However, very similar curves were obtained for measurements with optically thick clouds. Our results have been smoothly joined with the temperature gradients found above and below our region of sensing. Figure 2 also indicates the location of the regions probed in our measurement, at radio wavelengths, and within the 7.7-  $\mu$ m CH<sub>4</sub> band. The temperature values found from these various determinations are quite consistent near their boundaries. The temperature gradient becomes adiabatic at the higher-pressure domain of our sensing region, which is consistent with the temperature lapse rate implied by the radio results. We find that the lapse rate first reaches the adiabatic value and therefore that the convection zone begins at approximately 0.4 atm. This result is in good agreement with the theoretical predictions of Pollack and Ohring (13), which were based on a radiative equilibrium model. Our measurements also suggest the presence of a temperature minimum and the start of an inversion layer at the lower-pressure levels of our region. This aspect of the temperature profile is suggested by the small displacement of the observed minimum in our brightness temperature spectrum from the center of the J = 1 H<sub>2</sub> rotational transitions. These results are in accord with Orton's analysis (8) of measurements made in a spectral region containing the 7.7- $\mu$ m fundamental of CH<sub>4</sub>. The value of our temperature minimum (115°K) is also in good agreement with Orton's value of about 118°K.

The temperature profiles shown in Fig. 2 are in conflict with the structure found from a preliminary analysis of the Pioneer 10 S-band occultation experiment (14). The results from the occultation experiment indicate a much warmer atmosphere than our results at pressures above several millibars. Our infrared observations could be reconciled with the S-band data if we



Fig. 2. A plot of the derived pressure-temperature profile for the Jovian atmosphere. The pressure level most directly measured by various observational techniques is shown.

postulate the presence of an optically thick cloud near the 1-mbar region. However, in this case the pressure-induced opacity of  $H_2$  would be negligible and we would not expect to detect the J = 0 and J = 1 rotational transitions in our spectrum. The presence of these features in our spectrum suggests that further study of the S-band occultation results is needed. These conclusions are also supported by the consistency of our temperature profile with values obtained at shorter infrared wavelengths and in the radio domain, as discussed above.

For models containing no NH<sub>3</sub> cloud opacity in the zones of Jupiter, we find that the  $\alpha_{H_2}$  is 0.85  $\pm$  0.07, whereas we obtain a value of 1.0  $^{+0}_{-0.04}$  for the cases involving an optically thick NH<sub>3</sub> cloud. These error bars reflect only the formal random errors of our results. The cloud-free models had a smaller value for the minimum fractional flux residual than the set incorporating a thick cloud (0.039 versus 0.043). Combining the above two estimates, we conclude that  $\alpha_{H_2}$  equals 0.89  $\pm$  0.11. This range of values encompasses the solar value of 0.86.

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## Cyclic Octatomic Sulfur: A Possible Infrared and Visible Chromophore in the Clouds of Jupiter

Abstract. A brown polymeric material, produced under simulated Jovian conditions, is composed primarily of cyclic octatomic sulfur, although a range of complex organic compounds is also present. The polymeric sulfur, produced from the ultraviolet photolysis of hydrogen sulfide, exhibits its strongest band at 465 reciprocal centimeters, in fair agreement with the frequency of the unidentified Jovian absorber recently announced by Houck et al. Polymeric octatomic sulfur may be an important constituent of the Jovian clouds.

Near-ultraviolet (near-UV) light is known to be an effective agent for the photoproduction of a range of organic molecules from simulated primitive Earth and contemporary Jovian environments (1, 2). In the course of such experiments, a complex powdery polymeric material is produced, which, we have suggested (2), may be related to the molecular chromophores responsible for the coloration in the clouds of Jupiter. In this report we discuss the infrared spectrum of this powder and its comparison with recent high-altitude infrared spectra of Jupiter.

In a typical experiment, a spherical reaction vessel with a capacity of 12.7 liters is filled with 3350 cm<sup>3</sup> of CH<sub>4</sub>, 3437 cm<sup>3</sup> of NH<sub>3</sub>, and 2862 cm<sup>3</sup> of H<sub>2</sub>S, and the gases are irradiated with the resonance emission lines of mercury from a 450-watt highpressure quartz lamp (Hanovia) radiating 5.8 watts at 2537 Å. The gases, along with the photolytic products, are recycled by a greaseless solenoid pump (Watson) out from and back into the reaction vessel. (Both CH<sub>4</sub> and NH<sub>3</sub> have been observed spectroscopically in the Jovian atmosphere, and, in an excess of H<sub>2</sub>, H<sub>2</sub>S is expected to be present.) As the photolysis continues, the interior walls of the reaction vessel accumulate an orange-brown precipitate. After 12 hours and 40 minutes of



Fig. 1. The infrared spectra of the brown polymeric material (bottom) and sulfur (top). The additional absorption features in the experimental product are due to a variety of organic compounds.

photolysis, 3521 cm<sup>3</sup> of  $C_2H_6$  (now known to be a minor constituent of the Jovian atmosphere) and an additional 850 cm<sup>3</sup> of  $H_2S$  are introduced. After 29 hours of further photolysis, a seal is magnetically broken, permitting the pump to circulate gases and reaction products over an NH<sub>4</sub>OH bath (corresponding to the proposed lower clouds of Jupiter). After another 6 days and 19 hours, 1150 cm<sup>3</sup> of  $H_2S$  are introduced. The experiment is terminated after an additional 8 days and 22 hours. The visual appearance of the brownish powder did not change after the first few hours of photolysis. The NH<sub>4</sub>OH bath, which was not exposed to UV radiation, also acquired a distinct brownish coloration after the reaction products acquired access to it. Additional H<sub>2</sub>S was introduced because this molecule is the primary photon acceptor in such experiments; its photolysis produces hot hydrogen atoms superthermal by several electron volts, which initiate subsequent steps of the reactions. Solar near-UV photons are calculated to reach atmospheric levels on Jupiter at which H<sub>2</sub>S photolysis will proceed. In such experiments a wide variety of organic molecules are produced, including upon hydrolysis more than 40 amino acids, among them cystine (1-3).

In our earlier experiments, the polymer was separated by paper chromatography into two components, one described as "brown" and the other as "yellow." The yellow material is a complex mixture of organic compounds with negligible elemental sulfur, as determined, for example, by mass spectrometry. The brown material must contain large quantities of sulfur and its compounds. Clear mass spectrometric evidence of polymeric sulfur from  $S_1$  to  $S_8$ was secured for an evaporated aliquot of the aqueous bath. We have now examined the properties of the full polymeric powder, not subjected to either chromatographic separation or organic chemical extraction techniques. After hydrolysis of the full polymer with 6N HCl an atomic analysis (4) of the residue gives the following abundances (in percent by weight): hydrogen, 0.15; carbon, 1.44; oxygen, 1.89; nitrogen, 0.42; and sulfur, 95.99. The residue is clearly primarily sulfur.

A few milligrams of our raw precipitate were scraped from the wall of the reaction vessel and mixed with about 250 mg of CsI powder in a stainless steel vial with a stainless steel ball pestle. Grinding was accomplished in 2 minutes with an electric mixer. The mixed powder appeared brownish. It was then transferred to a die assembly which was pumped for 10 minutes to remove water vapor. A pressure of 1700 atm was then applied for 10 minutes, and the press repeated twice. Figure 1 shows the in-